and azoisobutyronitrile (3.24 g.) were refluxed in 30 ml. of benzene for 8 hr. under nitrogen. The benzene and tetramethylsuccinonitrile were removed by steam distillation. The yellow residue was dissolved in benzene, dried, and the solvent was removed by heating on the steam-bath for 1 hr. *in vacuo*. The yellow glass which resulted (1.82 g.) did not form a crystalline picrate. Seeding of 187 mg. of this material in benzene–absolute ethanol with a crystal of dihydro-bis-(cyanopropyl)-benzpyrene (X, m.p. 222–224°) yielded 10 mg. of white crystals, m.p. 220–224°.

Dehydrogenation of the yellow glass with sulfur at 215° and with 10% palladium–charcoal at 315° yielded benzpyrene as the sole identifiable product. Dehydrogenation with chloranil in boiling xylene for 47 hr. yielded an impure sample of X.

Dehydrogenation of Dihydro-bis-(cyanopropyl)-benzpyrene (X).—The bis-compound X (29 mg., m.p. 208–220°) was mixed with 4 mg. of 10% palladium–charcoal and heated under nitrogen at 315° for 1 hr. in a sublimation apparatus. The sublimate was rinsed into the apparatus with benzene, the benzene was removed on the steam-bath, and the material was heated at 315° for 1 hr. more. The mixture was dissolved in benzene, filtered and was concentrated on the steam-bath under nitrogen. The residue could not be recrystallized from benzene–hexane; it was therefore sublimed at 140–165° (0.1 mm.), and the yellow sublimate (9.2 mg.) was recrystallized from benzene–hexane. The yellow crystals obtained (4.5 mg.) melted at 176–178° and gave no depression on mixed m.p. with authentic benzpyrene.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

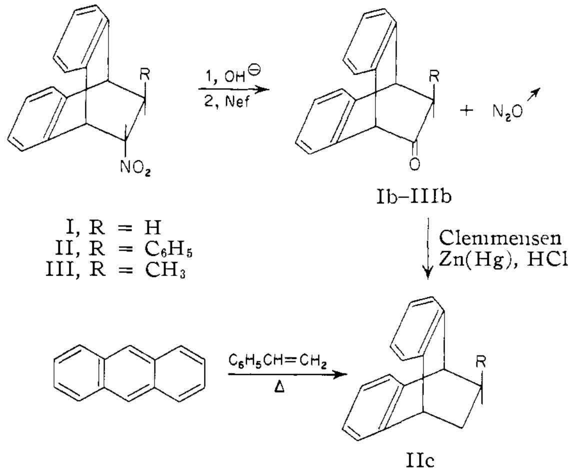
The Nef Reaction on 9,10-Dihydro-(11-nitroethano)-anthracenes. A New Route to 9,10-Dihydro-(11-ketoethano)-anthracenes[1]

BY WAYLAND E. NOLAND, M. SCOTT BAKER AND HOWARD I. FREEMAN

RECEIVED NOVEMBER 14, 1955

The application of the Nef reaction to the salts of the three most readily available secondary nitro 9,10-dihydro-9,10-ethanoanthracenes is reported. Two of the ketones corresponded in physical properties to samples previously prepared by other methods; the third was previously unknown. It was converted by Clemmensen reduction to a hydrocarbon, 9,10-dihydro-9,10-(11-phenylethano)-anthracene, which was synthesized independently by the Diels–Alder reaction of anthracene with styrene, thus establishing that no rearrangement had taken place during the formation of the ketone.

The preparation of 9,10-dihydro-9,10-(11-nitroethano)-anthracenes by the Diels–Alder reaction of anthracene with nitroölefins has been previously described.[2] Salts of the three secondary nitro adducts (I–III) obtained in the best yields have been found to undergo the Nef reaction,[3] yielding the corresponding ketones Ib–IIIb



I, R = H
II, R = C_6H_5
III, R = CH_3

The Nef reaction on the potassium salt of I gave the corresponding ketone Ib in 87% crude yield. This, and its oxime, were identical with the corresponding compounds prepared by Wawzonek and Hallum[4] through a series of reactions from anthracene and methyl acrylate or vinyl acetate. The ketone IIb was isolated in 56% crude yield as the 2,4-dinitrophenylhydrazone and in 26% yield in free form, along with a large amount of an amorphous product. The ketone IIIb was obtained in 17% yield, along with nitrogen-containing products. The infrared spectrum and melting point of IIIb corresponded to those of the sample obtained by Vaughan and Milton[5] from the action of 48% hydrobromic acid on 9,10-dihydro-9,10-(11-hydroxy-*cis*-11,12-dicarboxyanhydro-12-methylethano)-anthracene. The lower yields of IIb and IIIb relative to Ib, and the presence of nitrogen-containing products in the former cases, suggest that neighboring methyl or phenyl groups may sterically hinder the Nef reaction on carbon and cause reaction on nitrogen to be relatively more favored.

The best yields of ketones were obtained in the present work by gradually adding acid to cold methanolic alkaline solutions of the nitro compounds, using ether to keep the organic reactants in solution. Gradual addition of acid permits the reaction to pass through a wide range of acidities, including whichever is most favorable to the Nef reaction. Reversal of the method by adding an alkaline solution of the nitro compound to acid generally gave lower yields of ketone; high initial acidity did not seem to favor the Nef reaction. Gradual addition of a methanolic alkaline solution of III to cold hydrochloric acid and ether gave only an 11% yield of the ketone IIIb, a higher yield of a

---

[1] From the M.S. theses of Howard I. Freeman (on training assignment from the U. S. Air Force Institute of Technology), December 1953, and M. Scott Baker, June 1955, and from work by the senior author, 1953–1955. Paper presented before the Organic Division at the 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept. 16, 1955.

[2] (a) W. E. Noland, H. I. Freeman and M. S. Baker, THIS JOURNAL, **78**, 188 (1956); (b) K. Klager, *J. Org. Chem.*, **20**, 650 (1955).

[3] W. E. Noland, *Chem. Revs.*, **55**, 137 (1955).

[4] S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).

[5] W. R. Vaughan and K. M. Milton, THIS JOURNAL, **74**, 5623 (1952).

nitrogen-containing product, m.p. 134–135.5°, and a 56% yield of an oxime.[6]

The Nef reaction occurs normally with the 2-nitrobicyclo[2,2,1]heptanes,[7] but all attempts to carry out Nef reactions with the corresponding unsaturated compounds, the 5-nitrobicyclo[2,2,1]-2-heptenes, have failed.[7,8] The Nef reaction proceeds normally, however, with the next higher homolog, 5-nitrobicyclo[2,2,2]-2-octene.[9] The present work shows that the reaction also occurs with the 7-nitrobicyclo[2,2,2]-2,5-octadienes, where aromatic unsaturation is present in the corresponding positions.

The ketones Ib–IIIb have ultraviolet spectra which represent the superposition of spectra of typical dihydroanthracenes[2a] on the band spectra of cyclic ketones.[10] The intensities of the two strongest ketone bands, however, are about 40 times greater than with cyclohexanone, and there is a shift toward longer wave lengths, from 285 and 292[10] to 298–302 and 304–309 mμ. The shift is greatest in the case of IIb, as might be expected, since the intervening CH group is probably not sufficient to completely insulate the carbonyl group from the additional phenyl group. The 2,4-dinitrophenylhydrazones of Ib–IIIb have ultraviolet absorption maxima (see Experimental) in good agreement with those characteristic of unconjugated ketones,[11] in agreement with the structures assigned.

In order to provide a structural correlation similar to that available for Ib[4] and IIIb[5] and to establish that no rearrangement had taken place in its formation, the ketone IIb was converted by Clemmensen reduction in 15% yield to the hydrocarbon IIc, which was synthesized independently in 12% yield by the Diels–Alder reaction of anthracene with styrene. Two attempts to carry out the corresponding reaction of anthracene with *trans*-stilbene gave no adduct. Analogy exists in the fact that anthracene undergoes Diels–Alder reactions with several unsaturated hydrocarbons: indene in 94–96% yield,[12] 1,4-dihydronaphthalene in 34% yield,[13] ethylene[14] and cyclohexene.[14] Styrene, likewise, is known to act as a dienophile in Diels–Alder reactions with symmetrical[15] and unsymmetrical[16] dienes, but the yields are generally rather low, possibly because of competing polymerization of the styrene, even though in most cases inhibitors have been used.[15a,16]

Experimental

Melting points were determined on calibrated thermometers.

9,10-Dihydro-9,10-(11-ketoethano)-anthracene (Ib).—9,10-Dihydro-9,10-(11-nitroethano)-anthracene (0.271 g., 0.00108 mole) and a saturated solution of potassium hydroxide in ethanol (15 cc.) were allowed to stand for 1.5 hours until solution was practically complete. The solution was filtered and cooled in an ice-bath. Cold concentrated hydrochloric acid was added dropwise, with stirring, to a *p*H of about 2. A white precipitate formed immediately upon addition of the acid and the solution developed a bluish green color as it became acidic. Cold aqueous potassium hydroxide solution was added dropwise to a *p*H of about 10. The bluish green color vanished upon basification and the solution became yellow, while the precipitate persisted. The mixture was alternately slowly acidified to a *p*H of about 2 and basified to a *p*H of about 10 until the bluish green color no longer developed upon acidification. This required a total of four acidifications.

The cold mixture was then warmed on a steam-bath for 0.5 hour, and diluted with hot water (250 cc.), causing the precipitate to dissolve. The solution was allowed to stand for 12 hours, producing crystals (0.207 g., 0.000940 mole, 87%). Three recrystallizations from light petroleum (b.p. 60–68°) and sublimation at atmospheric pressure yielded fluorescent white crystals of 9,10-dihydro-9,10-(11-ketoethano)-anthracene (0.118 g., 0.000536 mole, 50%), m.p. 151–152.5°; reported m.p. 152.5–153°.[4] Mixed m.p. with an authentic sample[17] was 153–153.5°. The infrared spectra were identical; $\nu_{C=O}$ (cm.$^{-1}$) 1731 in CCl_4, 1725 in $CHCl_3$. λ_{max} in 95% C_2H_5OH: 254 mμ inflection (log ε 2.84), 261 inflection (2.96), 267 (3.05), 274 (3.05), 298 (2.86), 304 inflection (2.85)

Oxime of Ib: m.p. 212–214°; reported m.p. 214–214.5°.[4] Mixed m.p. with an authentic sample[17] was 212–215°. The infrared spectra were identical; $\nu_{C=N}$ (cm.$^{-1}$) 1659 in Nujol; λ_{max} in 95% C_2H_5OH: 252 mμ inflection (log ε 2.86), 259 (3.00), 266 (3.14), 273 (3.20). Molecular weight by the Rast method: calcd. 235, found 240.

2,4-Dinitrophenylhydrazone of Ib.—9,10-Dihydro-9,10-(11-ketoethano)-anthracene (0.060 g., 0.000273 mole) was added to a solution of 2,4-dinitrophenylhydrazine (0.106 g., 0.000535 mole) and concentrated sulfuric acid (0.5 cc.) in ethanol (3.5 cc.) and the solution was warmed on a steam-bath. The precipitate (0.0931 g., 0.000232 mole, 85%), which formed within about 3 minutes, was dissolved in chloroform and chromatographed on alumina. The column was developed with chloroform and eluted with solutions of light petroleum (b.p. 60–68°) in chloroform. Recrystallization of the eluted material from chloroform–petroleum (b.p. 90–100°) yielded the yellow 2,4-dinitrophenylhydrazone of 9,10-dihydro-9,10-(11-ketoethano)-anthracene, m.p. 214.5–216°; ν_{NH} (cm.$^{-1}$) 3340 in $CHCl_3$ and Nujol; $\nu_{C=N}$ (cm.$^{-1}$) 1621 in $CHCl_3$, 1618 in Nujol; λ_{max} in 95% C_2H_5OH: 363 mμ (log ε 4.36); in $CHCl_3$: 365 (4.40).

---

(6) Oximes have been reported previously as by-products of Nef reactions with secondary nitro compounds: (a) E. M. Nygaard, J. H. McCracken and T. T. Noland (to Socony Mobil Oil Co.), U. S. Patent 2,370,185 (Feb. 27, 1945); (b) E. M. Nygaard (to Socony Mobil Oil Co.), U. S. Patent 2,401,267 (May 28, 1946). Oximes have also been isolated from the decomposition of nitronic acids derived from secondary nitro compounds; (c) M. Konovalov, *Chem. Ber.*, **29**, 2193 (1896); (d) E. P. Kohler and J. F. Stone, Jr., THIS JOURNAL, **52**, 761 (1930); (e) D. A. Isăcescu, *Bul. soc. chim. România*, **18A**, 63 (1936) [*C. A.*, **31**, 3036 (1937)]. It should be noted that methanol was present in the reaction described in the present work. Secondary nitronic acids boiled with methanol have been known to yield oximes and the corresponding oxidation product, formaldehyde; (f) E. B. Hodge, THIS JOURNAL, **73**, 2341 (1951). The thermal decomposition of methyl secondary nitronates is known to yield the corresponding oximes and formaldehyde[d,e]; (g) C. D. Nenitzescu and D. A. Isăcescu, *Bul. soc. chim. România*, **14**, 53 (1932) [*Chem. Zentr.*, **104**, I, 1114 (1933)]; (h) F. Arndt and J. D. Rose, *J. Chem. Soc.*, 1 (1935); (i) J. T. Thurston and R. L. Shriner, *J. Org. Chem.*, **2**, 183 (1937).

(7) (a) E. E. Van Tamelen and R. J. Thiede, THIS JOURNAL, **74**, 2615 (1952); (b) W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952).

(8) W. E. Parham, W. T. Hunter and R. Hanson, THIS JOURNAL, **73**, 5068 (1951).

(9) W. C. Wildman and D. R. Saunders, *J. Org. Chem.*, **19**, 381 (1954).

(10) G. Forster, R. Skrabal and J. Wagner, *Z. Elektrochem.*, **43**, 290 (1937).

(11) (a) G. D. Johnson, THIS JOURNAL, **75**, 2720 (1953); (b) H. Reich, K. F. Crane and S. J. Sanfilippo, *J. Org. Chem.*, **18**, 822 (1953).

(12) E. Mameli, A. Pancotto and V. Crestani, *Gazz. chim. ital.*, **67**, 669 (1937) [*C. A.*, **32**, 4571, 6647 (1938)].

(13) C. D. Hurd and L. H. Juel, THIS JOURNAL, **77**, 601 (1955).

(14) C. L. Thomas (to Universal Oil Products Co.), U. S. Patent 2,406,645 (Aug. 27, 1945) [*C. A.*, **41**, 487 (1947)]. It seems probable that the two isomers obtained from cyclohexene with anthracene result from *cis*- and *trans*-fusion of the cyclohexane ring, although proof is lacking.

(15) (a) K. Alder and H. F. Rickert, *Chem. Ber.*, **71**, 379 (1938); (b) V. S. Abramov and Ts. L. Mitropolitanskaya, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 207 (1940) [*C. A.*, **34**, 7284 (1940)]; (c) B. A. Arbuzov and D. A. Akmed-Zade, *J. Gen. Chem.* (*U.S.S.R.*), **12**, 212 (1942) [*C. A.*, **37**, 2733 (1943)]; (d) Velsicol Corp., British Patent 614,931 (Dec. 30, 1948) [*C. A.*, **43**, 4693 (1949)]; S. H. Herzfeld, R. E. Lidov and H. Bluestone (to Velsicol Corp.), U. S. Patent 2,606,910 (Aug. 12, 1952) [*C. A.*, **47**, 8775 (1953)].

(16) (a) K. Alder and J. Haydn, *Ann.*, **570**, 201 (1950); (b) J. S. Meek, R. T. Merrow and S. J. Cristol, THIS JOURNAL, **74**, 2667 (1952).

(17) Kindly provided by Dr. Stanley Wawzonek.

Anal. Calcd. for $C_{22}H_{16}N_4O_4$ (400.38): C, 65.99; H, 4.03; N, 13.99. Found: C, 65.72; H, 4.13; N, 13.58.

9,10-Dihydro-9,10-(11-keto-12-phenylethano)-anthracene (IIb).—9,10-Dihydro-9,10-(*trans*-11-nitro-12-phenylethano)-anthracene (4.47 g., 0.01365 mole) was dissolved by refluxing with a solution containing 70% aqueous potassium hydroxide (150 cc.) and methanol (250 cc.). The solution was cooled in an ice-bath and an ice-cold mixture of concentrated sulfuric acid (425 g.), water (275 cc.) and ether (600 cc.) was added slowly, with stirring. A green color went into the ether layer and was still present 3.5 hours after the first addition of acid. A white precipitate remained in the aqueous layer but dissolved upon the addition of cold water. The ether layer was separated and the aqueous layer was extracted several times with ice-cold ether and light petroleum (b.p. 60–68°). The combined organic solutions were washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvents at room temperature under reduced pressure left an amorphous, yellowish brown solid (4.84 g.). This solid was dissolved in benzene (50 cc.) and chromatographed on alumina (250 g.). The column was developed and eluted with light petroleum (b.p. 60–68°), followed by solutions (1 l.) containing increasing amounts of anhydrous ether, giving a small amount of green oil. Elution with 70% anhydrous ether–30% light petroleum (b.p. 60–68°) and 100% anhydrous ether yielded a product (1.05 g., 0.00355 mole, 26%), m.p. 149–156°. Several recrystallizations, with charcoal, from light petroleum (b.p. 60–68°) yielded fluorescent fine white needles of 9,10-dihydro-9,10-(11-keto-12-phenylethano)-anthracene, m.p. 157–159°; $\nu_{C=O}$ (cm.$^{-1}$) 1733 in CCl_4; λ_{max} in 95% C_2H_5OH: 252 mμ (log ϵ 3.17), 259 (3.15), 265 (3.19), 273 (3.14), 302 (2.81), 309 (2.81). (Great difficulty was encountered in freeing the ketone from impurities having anthracenoid absorption at longer wave lengths and intense bands at 252–254, 273–274 and 322–323 mμ. The best sample, the ultraviolet absorption of which is reported here, was unreacted ketone recovered from the Clemmensen reduction. It was still possibly slightly contaminated, as suggested by the intensity of the band at 252 mμ.)

Anal. Calcd. for $C_{22}H_{16}O$ (296.35): C, 89.16; H, 5.44. Found: C, 89.03; H, 5.32.

Final elution with methanol gave an amorphous brown solid (2.89 g.).

2,4-Dinitrophenylhydrazone of IIb. A. By the Nef Reaction without Isolation of the Ketone IIb.—9,10-Dihydro-9,10-(*trans*-11-nitro-12-phenylethano)-anthracene (1.00 g., 0.00306 mole) was dissolved in a solution of Claisen alkali [20 cc., made from potassium hydroxide (350 g.) and water (250 cc.) diluted to 1 l. with methanol], water (20 cc.) and methanol (10 cc.). The solution was cooled in an ice-bath and an ice-cold mixture of concentrated sulfuric acid (31 g.), water (31 g.) and ether (29 g.) was added in small portions, with shaking. A white precipitate formed immediately and, as the addition was continued, a greenish ethereal layer appeared. The mixture was shaken for about 0.75 hour and left in the ice-bath for several hours. Ice-cold water and ether were then added and the aqueous layer was extracted several times with ice-cold ether. The combined ether solutions were washed with water and evaporated under reduced pressure, leaving a white solid. This white solid was dissolved in ethanol (30 cc.) and a warm solution of 2,4-dinitrophenylhydrazine (0.60 g., 0.00303 mole) and concentrated sulfuric acid (3.0 cc.) in water (4.5 cc.) and ethanol (15 cc.) was added. The resulting solution was warmed on a steam-bath for 0.5 hour and then set aside for several days. A precipitate (1.5 g.) formed, consisting of an amorphous red solid and an amorphous yellow solid. Recrystallization, with charcoal, from ethanol–water gave an amorphous yellow solid (0.81 g., 0.00170 mole, 56%), m.p. 130–140° (indefinite, with decomposition). Further recrystallization, with charcoal, from ethanol gave the yellow, powdery 2,4-dinitrophenylhydrazone of 9,10-dihydro-9,10-(11-keto-12-phenylethano)-anthracene, m.p. 187.5–189° (indefinite, with decomposition); ν_{NH} (cm.$^{-1}$) 3270 in CCl_4, 3260 in Nujol; $\nu_{C=N}$ (cm.$^{-1}$) 1611 in CCl_4, 1610 in Nujol; λ_{max} in 95% C_2H_5OH: 363 mμ (log ϵ 4.37); in $CHCl_3$: 367 mμ (4.39).

Anal. Calcd. for $C_{28}H_{20}N_4O_4$ (476.47): C, 70.58; H, 4.23; N, 11.76. Found: C, 70.53, 70.05; H, 4.55, 4.30; N, 11.73.

B. From the Ketone IIb.—The infrared spectrum of the 2,4-dinitrophenylhydrazone prepared from 9,10-dihydro-9,10-(11-keto-12-phenylethano)-anthracene was identical with that of the sample described in Part A.

9,10-Dihydro-9,10-(11-phenylethano)-anthracene (IIc). A. By the Diels–Alder Reaction of Anthracene with Styrene.—Fluorescent grade[18] anthracene (39.5 g., 0.222 mole), freshly distilled styrene (11.9 g., 0.114 mole, n^{26}D 1.5440), twice recrystallized *p-t*-butylcatechol (1 g.) and xylene (425 cc.) were shaken in an autoclave for four hours. The temperature was allowed initially to rise to 275° and thereafter was maintained at 190–210°. After the mixture had cooled to room temperature, the precipitated anthracene was filtered off and the filtrate evaporated at room temperature, leaving a brown sticky residue. The residue was dissolved in boiling benzene and more anthracene crystallized out upon cooling. After evaporation of the benzene, the residue, in 1-g. portions, was dissolved in light petroleum (b.p. 60–68°) and chromatographed on alumina (100 g.) packed wet with light petroleum (b.p. 28–38°). The chromatograms were developed with light petroleum (b.p. 28–38°) and eluted with mixtures of light petroleum (b.p. 28–38° and 60–68°). The small, fluorescent first band contained anthracene, and was discarded. The next band, also fluorescent under ultraviolet light, contained the product (3.84 g., 0.0136 mole, 12%), m.p. 94–97°. Two recrystallizations from ethanol yielded white chunky crystals of 9,10-dihydro-9,10-(11-phenylethano)-anthracene, m.p. (softens at 96°) 99.5–100.5°; λ_{max} in 95% C_2H_5OH: 253 mμ inflection (log ϵ 2.93), 259 (3.05), 265 (3.18), 272 (3.23).

Anal. Calcd. for $C_{22}H_{18}$ (282.36): C, 93.57; H, 6.43. Found: C, 93.52, 93.87; H, 6.75, 6.64.

B. By the Clemmensen Reduction of 9,10-Dihydro-9,10-(11-keto-12-phenylethano)-anthracene (IIb).—By the method of Martin[19] as modified by Bachmann and Edgerton[20] for the Clemmensen reduction, 9,10-dihydro-9,10-(11-keto-12-phenylethano)-anthracene (0.50 g., 0.00169 mole) was dissolved in toluene (5 cc.) and added to freshly prepared zinc amalgam (10 g.). Concentrated hydrochloric acid (12 cc.) and glacial acetic acid (10 cc.) were added and the mixture was refluxed for 24 hours. Additional concentrated hydrochloric acid (10 cc.) and glacial acetic acid were added occasionally in small portions. A blue fluorescence appeared after about 12 hours and persisted during the remainder of the reflux period. The reaction mixture was cooled, water (60 cc.) and ether were added and the layers were separated The aqueous layer was extracted with ether until the ether extracts no longer fluoresced (8 times). The combined organic solutions were washed with water and evaporated under reduced pressure, leaving a brownish gum (0.39 g.), which fluoresced blue in strong daylight. This gum was dissolved in benzene and chromatographed on alumina (50 g.) packed wet with light petroleum (b.p. 60–68°). Elution with light petroleum (b.p. 60–68°) gave the product (0.07 g., 0.00025 mole, 15%), m.p. 94–96°. Recrystallization from methanol yielded white chunky crystals of 9,10-dihydro-9,10-(11-phenylethano)-anthracene, m.p. 97–99.5°, mixed m.p. with sample prepared in Part A, 97–99°. The infrared spectrum was identical with that of the sample prepared in Part A.

Further elution of the column with solutions of anhydrous ether and light petroleum (b.p. 60–68°) removed an oil (0.08 g.) having a strong blue fluorescence. Elution with anhydrous ether (100 cc.) gave unreacted ketone (0.20 g., 40%), m.p. 155–159° Two recrystallizations from light petroleum (b.p. 60–68°) gave white needles, m.p. 159–161°.

9,10-Dihydro-9,10-(11-keto-12-methylethano)-anthracene (IIIb).—9,10-Dihydro-9,10-(*trans*-11-nitro-12-methylethano)-anthracene (1.95 g., 0.00735 mole) was dissolved in Claisen alkali (60 cc.). The solution was cooled in an ice-bath and an ice-cold mixture of concentrated sulfuric acid (102 g.), water (204 g.) and ether (102 g.) was added dropwise, with stirring, during 1.75 hours. A green color developed in the reaction solution and was still present after a total of 4 hours of stirring with cooling in the ice-bath. Ice-cold water and ether were added and the layers were

---

[18] (a) J. A. C. Yule (to Eastman Kodak Co.), U. S. Patent 2,213,-755 (Sept. 3, 1940) [*C. A.*, **35**, 464 (1941)]; (b) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, 1941, p. 345, footnote 13.

[19] E. L. Martin, THIS JOURNAL, **58**, 1438 (1936).

[20] W. E. Bachmann and R. O. Edgerton, *ibid.*, **62**, 2550 (1940).

separated. The aqueous layer was extracted with ice-cold ether (10 times) and light petroleum (b.p. 60–68°) (3 times). The combined organic solutions were washed with water and evaporated under reduced pressure at room temperature, leaving a white residue, m.p. 109–121°, and a small amount of greenish residue. The combined residues were dissolved in benzene (50 cc.) and chromatographed on alumina (200 g.) packed wet with light petroleum (b.p. 60–68°). Elution gave the following fractions: (a) 60% anhydrous ether–40% light petroleum (b.p. 60–68°) gave a white solid (0.06 g.). Recrystallization from light petroleum yielded white chunky crystals, m.p. 194–194.5°. The infrared spectrum in Nujol showed a strong band at 1562 cm.$^{-1}$ and a moderately strong band at 1367 cm.$^{-1}$ λ in 95% C_2H_5OH: inflections at 252 mμ (5.91), 265 (4.78), 273 (4.14), where intensities are in E, g./l., 1 cm.

Anal. Calcd. for $C_{15}H_{14}N_2O_3$ (270.28): C, 66.65; H, 5.22; N, 10.37. Found: C, 66.25; H, 5.04; N, 10.21.

(b) 80–100% anhydrous ether–20–0% light petroleum (b.p. 60–68°) gave the product (0.30 g., 0.000128 mole, 17%), m.p. 108–114° Two recrystallizations from light petroleum (b.p. 60–68°) yielded fluorescent white needles of 9,10-dihydro-9,10-(11-keto-12-methylethano)-anthracene, m.p. 121.5–123°; reported: 121.6–122.4°,[5] $\nu_{C=O}$ (cm.$^{-1}$) 1730 in CCl_4, 1720 in Nujol. The infrared spectrum was identical with that[21] of a sample prepared by Vaughan and Milton[5]; λ_{max} in 95% C_2H_5OH: 253 mμ (log ϵ 2.84), 260 inflection (2.95), 267 (3.07), 273 (3.07), 299 (2.83), 305 (2.84).

Anal. Calcd. for $C_{17}H_{14}O$ (234.28): C, 87.15; H, 6.02. Found: C, 86.94; H, 6.22.

(c) Methanol gave unreacted nitro compound (0.82 g., 42%), m.p. 115–118°. Recrystallization from methanol gave white needles, m.p. 119.5–122.5°.

Addition of the Alkaline Solution of **9,10-Dihydro-9,10-**(*trans*-11-**nitro-12-**methylethano)-**anthracene to Acid. A.**—9,10-Dihydro-9,10-(11-nitro-12-methylethano)-anthracene (1.88 g., 0.00709 mole) was dissolved in Claisen alkali (40 cc.), cooled in an ice-bath and added dropwise to an ice-cold stirred mixture of concentrated hydrochloric acid (170 cc.), water (40 cc.) and ether (120 cc.), causing an immediate white precipitate. The mixture was stirred in the ice-bath for 4.5 hours, during which time the color changed from white to blue to greenish-yellow. Ice-cold water was added and the greenish ether layer was separated. The reddish aqueous layer was extracted with ice-cold ether (10 times) and light petroleum (b.p. 60–68°) (5 times). The combined organic solutions were washed with water (which removed the color from the organic layer and caused the water to become reddish) and evaporated under reduced pressure at room temperature, leaving a reddish brown residue. This residue was dissolved in benzene (25 cc.) and chromatographed on alumina (250 g.) packed wet with light petroleum (b.p. 60–68°). Elution gave the following fractions: (a) Solutions of anhydrous ether and light petroleum (b.p. 60–68°) gave a white solid (0.33 g.). Recrystallization from light petroleum (b.p. 60–68°) yielded white crystals, m.p. 134–135.5°. The infrared spectrum in Nujol showed a very strong band at 1554 cm.$^{-1}$ and a moderately strong band at 1345 cm.$^{-1}$ λ_{max} in 95% C_2H_5OH: 265 mμ (3.51), 273 (3.48), where intensities are in E, g./l., 1 cm.

Anal. Calcd. for $C_{19}H_{15}NO_5$ (337.32): C, 67.65; H, 4.48; N, 4.15. Found: C, 67.57; 67.67; H, 4.85, 4.71; N, 4.23.

(b) Anhydrous ether gave crude ketone (0.18 g., 0.00077 mole, 11%), m.p. 115–118°. Several recrystallizations from light petroleum (b.p. 60–68°) yielded white needles, m.p. 119.5–121.5°.

(c) Methanol gave a white solid (1.0 g., 0.0040 mole, 56%), m.p. 168–174°. Two recrystallizations, with charcoal, from methanol yielded white chunky crystals of an oxime, m.p. (sublimes) 173–175°; ν_{OH} (cm.$^{-1}$) 3580, 3280 in $CHCl_3$, 3270 in Nujol; $\nu_{C=N}$ (cm.$^{-1}$) 1660 in $CHCl_3$, 1655 in Nujol; λ_{max} in 95% C_2H_5OH: 252 mμ inflection (log ϵ 2.83), 259 (2.99), 266 (3.15), 273 (3.20).

Anal. Calcd. for $C_{17}H_{15}NO$ (249.30): C, 81.90; H, 6.06; N, 5.62. Found: C, 81.71, 81.65, 82.04; H, 6.26, 6.87, 6.10; N, 5.72, 5.65.

B.—The procedure of Part A was repeated, except that, instead of being chromatographed, the reddish brown residue was triturated with boiling light petroleum (b.p. 60–68°), leaving another reddish residue. The yellow extracts were boiled with charcoal and evaporated, leaving a whitish solid residue (1.5 g.) above a yellow oil. The whitish solid residue was triturated with light petroleum, and the extracts were boiled with charcoal, concentrated and cooled, giving rosettes of whitish crystals. Several recrystallizations from light petroleum yielded very fine white needles of the **oxime** of **9,10-dihydro-9,10-**(11-**keto-12-methylethano**)-**anthracene**, m.p. (sublimes) ~ 164–166° (broad and indefinite); ν_{OH} (cm.$^{-1}$) 3220 in Nujol; $\nu_{C=N}$ (cm.$^{-1}$) 1651 in Nujol. The infrared spectrum was identical with that of the oxime prepared from the ketone, but was clearly distinguishable from that of the oxime obtained in Part A; λ_{max} in 95% C_2H_5OH: 252 mμ inflection (log ϵ 2.89), 259 (3.04), 266 (3.18), 273 (3.23).

Anal. Calcd. for $C_{17}H_{15}NO$ (249.30): C, 81.90; H, 6.06; N, 5.62. Found: C, 82.14; H, 5.98; N, 5.83.

A sample of this oxime was dissolved in benzene and chromatographed on alumina packed wet with light petroleum (b.p. 60–68°). Elution with light petroleum removed nothing but elution with hydrous ether gave very fine white needles. Two recrystallizations, one with charcoal, from ethanol–water yielded very fine white needles of unchanged oxime, m.p. (sublimes) ~ 160–164° (broad and indefinite). The infrared and ultraviolet spectra were identical with those of the unchromatographed sample.

It seems probable that the oximes from Parts A and **B** are *syn* and *anti* isomers of each other, but they have not been interconverted, nor has the reason for obtaining two different compounds under apparently similar conditions been discovered.

Oxime of IIIb.—9,10-Dihydro-9,10-(11-keto-12-methylethano)-anthracene was refluxed with hydroxylamine hydrochloride and pyridine in ethanol solution for 3 hours. The crude oxime, obtained by evaporating off most of the ethanol and diluting the residue with water, was recrystallized from methanol–water and then sublimed at about 140° (2 mm.). The sublimate was recrystallized four times from light petroleum (b.p. 60–68°), yielding very fine white needles, m.p. (sublimes) ~ 158–161° (broad and indefinite). The infrared spectrum was identical with those of the samples from Part **B**, above.

2,4-Dinitrophenylhydrazone of IIIb.—Obtained by recrystallization from ethanol as fine red needles, m.p. (softens at 200°) 220–230° (indefinite, with decomposition); ν_{NH} (cm.$^{-1}$) 3300 in Nujol; $\nu_{C=N}$ (cm.$^{-1}$) 1614 in Nujol; λ_{max} in 95% C_2H_5OH: 363 mμ (log ϵ 4.37); in $CHCl_3$: 366 (4.40).

Anal. Calcd. for $C_{23}H_{18}N_4O_4$ (414.41): C, 66.66; H, 4.38; N, 13.52. Found: C, 66.51; H, 4.63; N, 13.70.

MINNEAPOLIS 14, MINN.

---

[21] Kindly provided by Dr. Wyman R. Vaughan.